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(54) **PHOTOELECTRIC CONVERSION DEVICE**

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(57) **ABSTRACT**

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To provide a photoelectric conversion device which has little light loss caused by light absorption in a window layer, the photoelectric conversion device includes a first electrode, a first semiconductor layer formed over the first electrode, a second semiconductor layer formed over the first semiconductor layer, a third semiconductor layer formed over the second semiconductor layer, and a second electrode formed over the third semiconductor layer; and the first semiconductor layer is a light-transmitting semiconductor layer containing an organic compound and an inorganic compound, and the second semiconductor layer and the third semiconductor layer are each a semiconductor layer containing an organic compound.

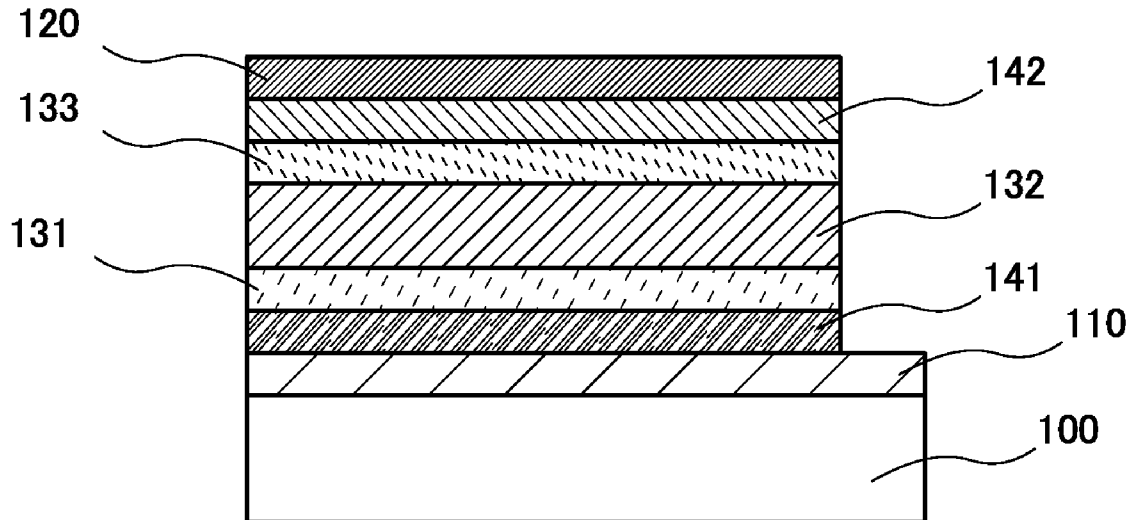


FIG. 1A

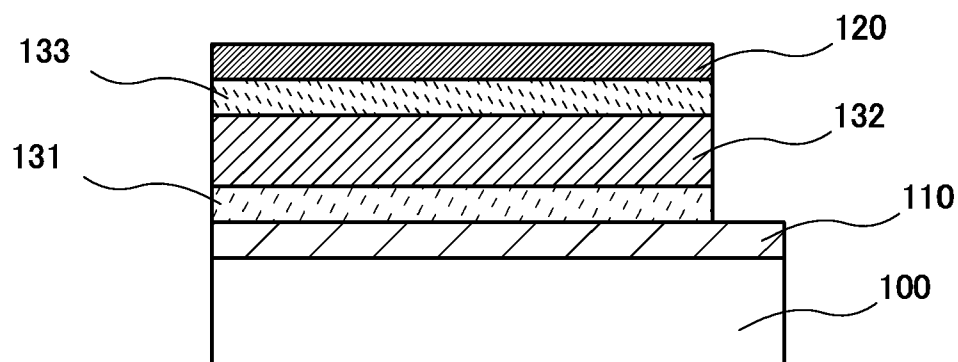


FIG. 1B

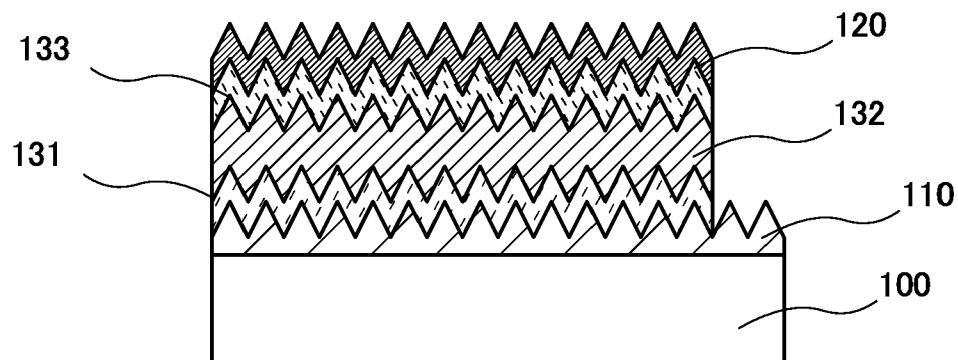


FIG. 2

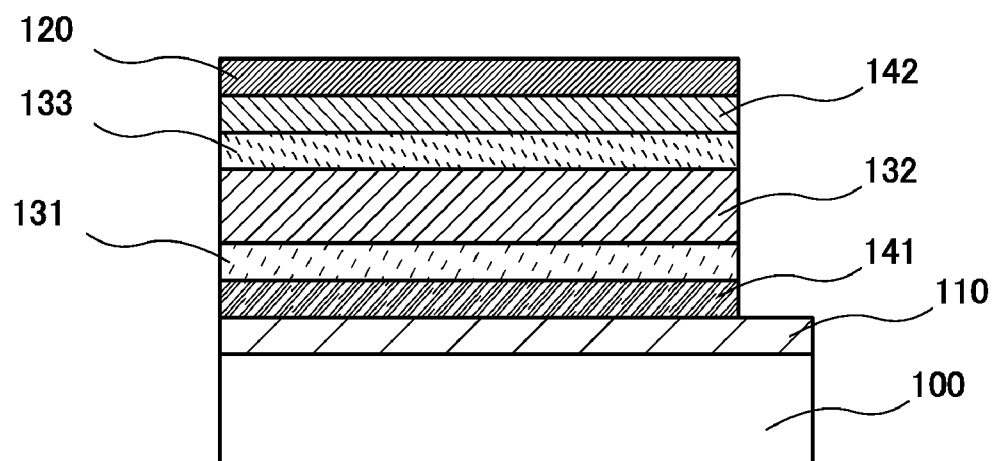


FIG. 3

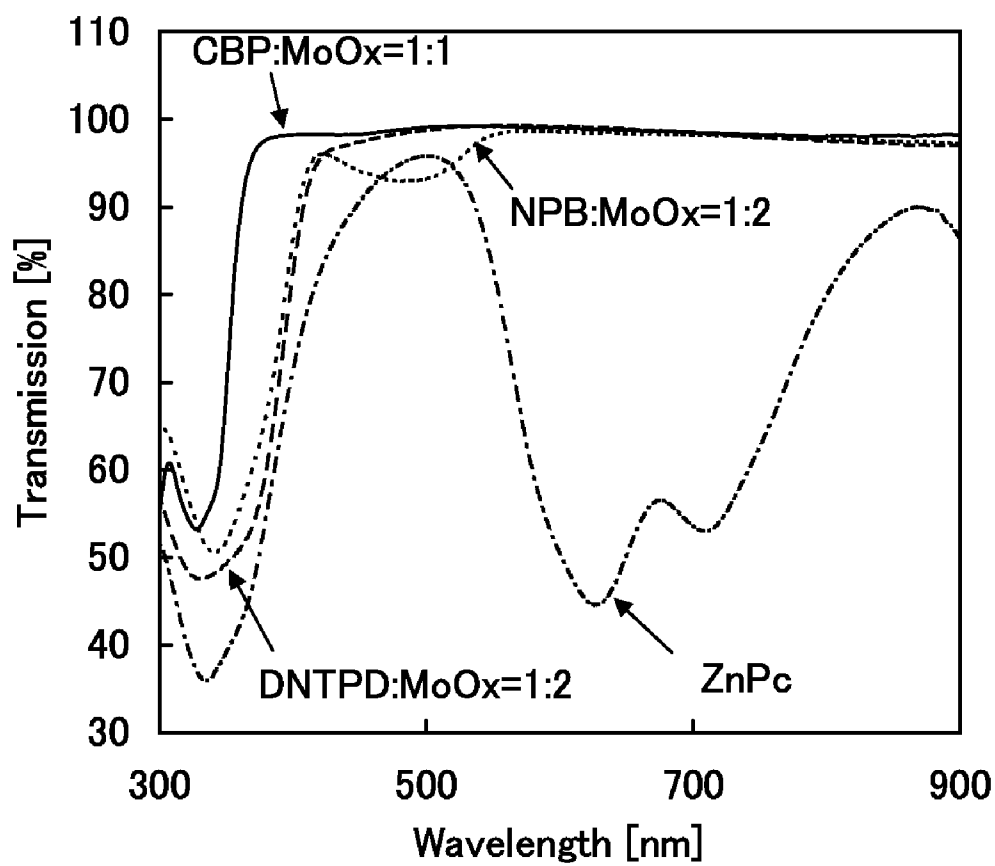
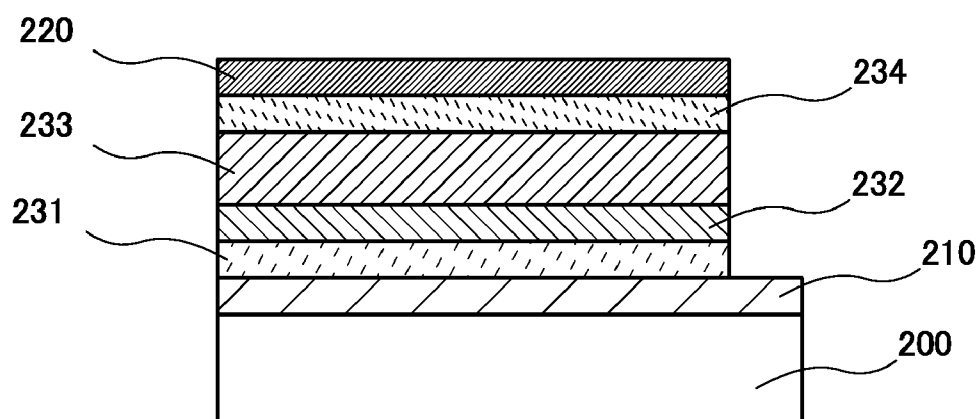


FIG. 4



PHOTOELECTRIC CONVERSION DEVICE

BACKGROUND OF THE INVENTION

[0001] 1. Field of the Invention

[0002] The present invention relates to a photoelectric conversion device in which a semiconductor including an organic material is used.

[0003] 2. Description of the Related Art

[0004] As a photoelectric conversion device which converts an optical energy into an electrical energy, a crystalline silicon solar cell such as a single crystalline silicon solar cell or a polycrystalline silicon solar cell, an amorphous silicon solar cell, and a compound semiconductor solar cell including CIGS (Cu(In,Ga)Se_2) and the like have been known. Although these solar cells are being widely used, there are still many problems in terms of cost and the like; thus, a solar cell that can be manufactured at low cost is desired. As one of solutions, a solar cell including an organic semiconductor has been suggested.

[0005] In addition to a dye-sensitized solar cell, a thin-film type solar cell has been known as an organic semiconductor solar cell. There is a thin-film type solar cell having a p-i-n junction structure, which includes phthalocyanine (H_2PC) that shows p-type semiconductor characteristics, a perylene pigment (Me-PTC) that shows n-type semiconductor characteristics, and a codeposited layer of the both (see Non-Patent Document 1). The thin-film type solar cell does not need such an electrolyte that is used in a dye-sensitized solar cell; therefore, there is an advantage that the productivity and long-term reliability can be controlled easily.

REFERENCE

[0006] [Non-Patent Document 1] M. Hiramoto, H. Fujiwara, M. Yokoyama, "Three-layered organic solar cell with a photoactive interlayer of codeposited pigments", Appl. Phys. Lett., 58, 1062-1064 (1991).

SUMMARY OF THE INVENTION

[0007] However, a thin-film type solar cell including an organic material has a problem in that the conversion efficiency thereof is lower than that of a silicon solar cell or a solar cell of another compound semiconductor.

[0008] Light loss caused by light absorption in a window layer can be given as one of the reasons that the conversion efficiency of the thin-film type solar cell does not improve. Although an exciton is generated also in the window layer by light absorption, the diffusion length thereof in an organic semiconductor is extremely short and thus the exciton is deactivated easily before reaching a junction. In other words, the light absorbed by the window layer is not substantially used; therefore, it is preferable to form the window layer with a material having a high light-transmitting property.

[0009] A conventional organic semiconductor used for a window layer has high resistance; therefore, the film thickness has needed to be small. Thus, there has been a problem in that a short circuit between upper and lower electrodes is likely to be caused by particles or the like.

[0010] Thus, an object of one embodiment of the present invention is to provide a photoelectric conversion device which has little light loss caused by light absorption in the window layer. Another object thereof is to provide a photoelectric conversion device in which a short circuit between upper and lower electrodes is less likely to be caused.

[0011] One embodiment of the present invention disclosed in this specification is a photoelectric conversion device including a p-type light-transmitting semiconductor layer which is formed using an organic compound and an inorganic compound as a window layer.

[0012] According to one embodiment of the present invention disclosed in this specification, a photoelectric conversion device includes a first electrode, a first semiconductor layer formed over the first electrode, a second semiconductor layer formed over the first semiconductor layer, a third semiconductor layer formed over the second semiconductor layer, and a second electrode formed over the third semiconductor layer; and the first semiconductor layer is a light-transmitting semiconductor layer containing an organic compound and an inorganic compound, and the second semiconductor layer and the third semiconductor layer are each a semiconductor layer containing an organic compound.

[0013] Note that in this specification and the like, ordinal numbers such as "first" and "second" are used in order to avoid confusion among components, and do not limit the order or number of the components.

[0014] In the above structure, the first semiconductor layer can have p-type conductivity, the second semiconductor layer can have i-type conductivity, and the third semiconductor layer can have n-type conductivity.

[0015] According to another embodiment of the present invention disclosed in this specification, a photoelectric conversion device includes a first electrode, a first semiconductor layer formed over the first electrode, a second semiconductor layer formed over the first semiconductor layer, a third semiconductor layer formed over the second semiconductor layer, a fourth semiconductor layer formed over the third semiconductor layer, and a second electrode formed over the fourth semiconductor layer; and the first semiconductor layer is a light-transmitting semiconductor layer containing an organic compound and an inorganic compound, and the second semiconductor layer, the third semiconductor layer, and the fourth semiconductor layer are each a semiconductor layer containing an organic compound.

[0016] In the above structure, the first semiconductor layer and the second semiconductor layer each can have p-type conductivity, the third semiconductor layer can have i-type conductivity, and the fourth semiconductor layer can have n-type conductivity.

[0017] Further, as the organic compound for forming the first semiconductor layer, any of an aromatic amine compound, a carbazole derivative, aromatic hydrocarbon, a high molecular compound, and a heterocyclic compound having a dibenzofuran skeleton or a dibenzothiophene skeleton can be used.

[0018] Furthermore, as the inorganic compound for forming the first semiconductor layer, any of a vanadium oxide, a niobium oxide, a tantalum oxide, a chromium oxide, a molybdenum oxide, a tungsten oxide, a manganese oxide, a rhenium oxide, and a titanium oxide can be used.

[0019] According to one embodiment of the present invention, a photoelectric conversion device which can reduce the light loss caused by light absorption in a window layer and has high conversion efficiency can be provided. Further, a photoelectric conversion device in which a short circuit between upper and lower electrodes is less likely to be caused can be provided.

BRIEF DESCRIPTION OF THE DRAWINGS

[0020] FIGS. 1A and 1B are cross-sectional views each illustrating a photoelectric conversion device according to one embodiment of the present invention.

[0021] FIG. 2 is a cross-sectional view illustrating a photoelectric conversion device according to one embodiment of the present invention.

[0022] FIG. 3 is a graph comparing a transmittance of a conventional material for a window layer with a transmittance of a material for a window layer according to one embodiment of the present invention.

[0023] FIG. 4 is a cross-sectional view illustrating a photoelectric conversion device according to one embodiment of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

[0024] Embodiments of the present invention will be described below in detail with reference to the accompanying drawings. However, the present invention is not limited to the description below, and it is easily understood by those skilled in the art that modes and details disclosed herein can be modified in various ways without departing from the spirit and the scope of the present invention. Therefore, the present invention is not construed as being limited to description of the embodiments. In the drawings for explaining the embodiments, the same portions or portions having similar functions are denoted by the same reference numerals, and description of such portions is not repeated in some cases.

Embodiment 1

[0025] In this embodiment, a photoelectric conversion device according to one embodiment of the present invention will be described.

[0026] Note that in this specification, an n-type semiconductor is a semiconductor having characteristics as an electron donor, and a p-type semiconductor is a semiconductor having characteristics as an electron acceptor. Both of the semiconductors contain an organic material.

[0027] FIG. 1A is an example of a cross-sectional view of a photoelectric conversion device according to one embodiment of the present invention. The photoelectric conversion device includes, over a light-transmitting substrate 100, a first electrode 110, a first semiconductor layer 131, a second semiconductor layer 132, a third semiconductor layer 133, and a second electrode 120. As the light-transmitting substrate 100, for example, a glass substrate can be used.

[0028] Although, in this embodiment, an example in which a light-transmitting conductive film is used for the first electrode 110 and a surface on the substrate 100 side serves as a light-receiving plane is described, a surface on the second electrode 120 side can serve as a light-receiving plane when a light-transmitting conductive film is used for the second electrode 120. When the first electrode 110 and the second electrode 120 are both formed using a light-transmitting conductive film, both of the surfaces can serve as a light-receiving plane. Note that when only the second electrode 120 side serves as a light-receiving plane, the substrate 100 does not necessarily have a light-transmitting property.

[0029] Without limitation to the structure illustrated in FIG. 1A, the first semiconductor layer 131 and the third semiconductor layer 133 may be interchanged with each other. Further, as illustrated in FIG. 2, a first buffer layer 141 may be provided between the first electrode 110 and the first semiconductor layer 131, and a second buffer layer 142 may be provided between the second electrode 120 and the third semiconductor layer 133. The buffer layer is effective in improving contact characteristics between the semiconductor layer and the electrode, and a metal oxide such as a zinc oxide, a nickel oxide, or a molybdenum oxide or a conductive macromolecule such as polyethylenedioxythiophene/polystyrenesulfonic acid (abbreviation: PEDOT/PSS), which has conductivity or semiconductor characteristics, can be used. Note that at least one of the first buffer layer 141 and the second buffer layer 142 may be provided. Further, the materials of the first buffer layer 141 and the second buffer layer 142 may be different from each other.

[0030] FIG. 1B illustrates an example in which a surface of the first electrode 110 is processed to have unevenness. The first semiconductor layer 131, the second semiconductor layer 132, the third semiconductor layer 133, and the second electrode 120 reflect the unevenness of the surface of the first electrode 110 as illustrated in FIG. 1B. On the surface processed to have unevenness, multiply-reflected light is incident, and the light obliquely propagates into a photoelectric conversion region; thus, the light pass length is increased. In addition, a so-called light trapping effect in which reflected light by the rear surface is totally reflected at the surface can occur.

[0031] Note that for the light-transmitting conductive film, the following can be used: an indium tin oxide, an indium tin oxide containing silicon, an indium oxide containing zinc, a zinc oxide, a zinc oxide containing gallium, a zinc oxide containing aluminum, a tin oxide, a tin oxide containing fluorine, a tin oxide containing antimony, graphene, or the like. The light-transmitting conductive film is not limited to a single layer, and may have a layered structure of different films.

[0032] The first semiconductor layer 131 can be formed using a light-transmitting semiconductor layer having p-type conductivity. The light-transmitting semiconductor layer according to one embodiment of the present invention is a composite material of an inorganic compound and an organic compound.

[0033] It is possible to use, as the inorganic compound, a transition metal oxide whose band gap is greater than or equal to 2 eV, preferably greater than or equal to 3 eV. It is particularly preferable that the inorganic compound be an oxide of a metal belonging to any of Group 4 to Group 8 in the periodic table.

[0034] For example, as the inorganic compound, a vanadium oxide, a niobium oxide, a tantalum oxide, a chromium oxide, a molybdenum oxide, a tungsten oxide, a manganese oxide, a rhenium oxide, or a titanium oxide can be used. Among these, a molybdenum oxide is particularly preferable because of its stability in the air, low hygroscopic property, and easiness to be treated.

[0035] As the organic compound, a material whose band gap is greater than or equal to 2 eV, preferably greater than or equal to 3 eV, is used.

[0036] The organic compound preferably has a high hole-transport property. Specifically, a substance having a hole mobility higher than or equal to 10^{-6} cm²/Vs is preferably used. Note that other than the above substance, any substance that has a property of transporting more holes than electrons may be used.

[0037] For example, as the organic compound, any of a variety of compounds such as an aromatic amine compound,

a carbazole derivative, an aromatic hydrocarbon, a high molecular compound (e.g., an oligomer, a dendrimer, or a polymer), and a heterocyclic compound having a dibenzofuran skeleton or a dibenzothiophene skeleton can be used.

[0038] With the use of the inorganic compound and organic compound described above, a composite material having a high light-transmitting property can be formed.

[0039] The transition metal oxide has an electron-accepting property; thus, a composite material of an organic compound having a high hole-transport property and such a transition metal has high carrier density and exhibits p-type semiconductor characteristics. Further, the composite material has high transmittance of light in a wide wavelength range from visible light region to infrared region. Furthermore, the refractive index of the composite material is close to that of a light-transmitting conductive film such as an indium tin oxide film, so that it is possible to use the composite material as an anti-reflection film by adjusting the film thickness as appropriate.

[0040] The composite material can be formed by a codeposition method. Further, it is also possible to use a coating method, a sol-gel method, or the like. By increasing a mol rate of the inorganic compound to the organic compound, an absorbance in the charge transfer region increases. That is, more molecules tend to be excited; however, a charge-transport property also depends on the combination of an organic compound and an inorganic compound. Therefore, the mol rate is to be determined as appropriate. The thickness of the composite material is preferably 1 nm to 50 nm.

[0041] In a conventional photoelectric conversion device including an organic semiconductor, for example, phthalocyanine having insufficient transmittance is used for a window layer; thus, the light loss caused by light absorption in the window layer occurs. On the other hand, according to one embodiment of the present invention, the composite material having a light-transmitting property is used for a window layer, whereby the light loss caused by light absorption in the window layer can be reduced, and photoelectric conversion can be efficiently performed in a light absorption region.

[0042] FIG. 3 shows results obtained by comparing transmittance of zinc phthalocyanine (ZnPc) which is an example of a conventional material for a window layer with transmittance of each of composite materials of an inorganic compound and an organic compound according to one embodiment of the present invention, which are a composite material of 4,4'-di(N-carbazolyl)biphenyl (abbreviation: CBP) and a molybdenum oxide (the mixture ratio: CBP: molybdenum oxide=1:1), a composite material of 4,4'-bis(N-{4-[N'-(3-methylphenyl)-N'-phenylamino]phenyl}-N-phenylamino)biphenyl (abbreviation: DNTPD) and a molybdenum oxide (the mixture ratio: DNTPD: molybdenum oxide=1:2), and a composite material of 4,4'-bis[N-(1-naphthyl)-N-phenylamino]biphenyl (abbreviation: NPB) and a molybdenum oxide (the mixture ratio: NPB: molybdenum oxide=1:2). The composite material of an inorganic compound and an organic compound according to one embodiment of the present invention has much higher transmittance than zinc phthalocyanine which is an example of a conventional material for a window layer, which suggests that the light loss caused by light absorption in the window layer can be reduced. Since the composite material has high transmittance of light in a wide wavelength range, the first semiconductor layer **131** can be formed thick, whereby the resistance in the horizontal direction can be reduced and a short circuit in a vertical direction which is

caused between, for example, upper and lower electrodes can be prevented. Further, in the case where the composite material is used as the window layer, the buffer layer in contact with the window layer, which is illustrated in FIG. 2, can be omitted because the window layer has low contact resistance with the first electrode.

[0043] The third semiconductor layer **133** can be formed using a semiconductor layer having n-type conductivity. The third semiconductor layer **133** is preferably formed with a thickness of 10 nm to 50 nm by a codeposition method, a coating method, a sol-gel method, or the like as appropriate. An organic compound having an electron-transport property is preferably used for the third semiconductor layer **133**, and more preferably, a chelate metal complex having a chelate ligand containing an aromatic ring, an organic compound having a phenanthroline skeleton, an organic compound having an oxadiazole skeleton, a perylene derivative, a naphthalene derivative, quinones, methyl viologen, fullerene, and the like are used. Specifically, there are tris(8-quinolinolato)aluminum (abbreviation: Alq₃), tris(4-methyl-8-quinolinolato)aluminum (abbreviation: Almq₃), bis(10-hydroxybenzo[h]quinolinato)beryllium (abbreviation: BeBq₂), bis(2-methyl-8-quinolinolato)(4-phenylphenolato)aluminum (abbreviation: BAq), bis[2-(2'-hydroxyphenyl)benzoxazolato]zinc (abbreviation: Zn(BOX)₂), bis[2-(2'-hydroxyphenyl)benzothiazolato]zinc (abbreviation: Zn(BTZ)₂), bathophenanthroline (abbreviation: BPhen), bathocuproine (abbreviation: BCP), 2-(4-biphenyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole (abbreviation: PBD), 1,3-bis[5-(4-tert-butylphenyl)-1,3,4-oxadiazol-2-yl]benzene (abbreviation: OXD-7), 2,2',2''-(1,3,5-benzenetriyl)-tris(1-phenyl-1H-benzimidazole) (abbreviation: TPBI), 3-(4-biphenyl)-4-phenyl-5-(4-tert-butylphenyl)-1,2,4-triazole (abbreviation: TAZ), 3-(4-biphenyl)-4-(4-ethylphenyl)-5-(4-tert-butylphenyl)-1,2,4-triazole (abbreviation: p-EtTAZ), phenyl-C₆₁ butyric acid methyl ester (abbreviation: PCBM), naphthalen-2,3,6,7-tetracarboxylicdianhydride (abbreviation: NTCDA), and the like. Note that the present invention is not limited to these. Further, among the above compounds, a perylene derivative, a naphthalene derivative, quinones, methyl viologen, fullerene, and the like easily generate electron carriers, and are a suitable compound group for the third semiconductor layer **133**.

[0044] The second semiconductor layer **132** can be formed using a semiconductor layer having i-type conductivity. The second semiconductor layer **132** can be formed by a codeposition method with the above organic semiconductor material having n-type conductivity and an organic semiconductor material having p-type conductivity. The second semiconductor layer **132** is preferably formed with a thickness of 1 nm to 1000 nm.

[0045] As a typical organic semiconductor material having p-type conductivity, the following materials can be given: phthalocyanine (abbreviation: H₂Pc), copper phthalocyanine (abbreviation: CuPc), zinc phthalocyanine (abbreviation: ZnPc), tin phthalocyanine (SnPc), vanadyl phthalocyanine (abbreviation: VOPc), 4,4',4''-tris(N,N-diphenylamino)triphenylamine (abbreviation: TDATA), 4,4',4''-tris[N-(3-methylphenyl)-N-phenylamino]triphenylamine (abbreviation: MTDATA), 1,3,5-tris[N,N-di(m-tolyl)amino]benzene (abbreviation: m-MTDAB), N,N'-diphenyl-N,N'-bis(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine (abbreviation: TPD), 4,4'-bis[N-(1-naphthyl)-N-phenylamino]biphenyl (abbreviation: NPB), 4,4'-bis[N-[4-di(m-tolyl)amino]phenyl-N-

phenylamino}biphenyl (abbreviation: DNTPD), 4,4',4''-tris (N-carbazolyl)triphenylamine (abbreviation: TCTA), polyethylenedioxythiophene/polystyrenesulfonic acid (abbreviation: PEDOT/PSS), poly(3-hexylthiophene) (abbreviation: P3HT), poly[2,1,3-benzothiadiazole-4,7-diyl-2,5-thiophenediyl(1-dodecyl-1H-pyrrole-2,5-diyl)-2,5-thiophenediyl] (abbreviation: PTPTB), poly{2,1,3-benzothiadiazole-4,7-diyl[4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophen-2,6-diyl]} (abbreviation: PCPTBT), poly[2-methoxy-5-(3,7-dimethyloctyloxy)-1,4-phenylenevinylene] (abbreviation: MDMO-PPV), ammonium perfluorooctanoate (abbreviation: APFO), an alternating copolymer of thienothiophene and benzothiophene, and the like. Note that the present invention is not limited to these. Among the above compounds, an aromatic amine compound typified by TDATA, MTDATA, m-MTDAB, TPD, NPB, DNTPD, TCTA, and the like easily generates a hole carrier and is preferable to be used as the organic semiconductor material having p-type conductivity.

[0046] A p-i-n junction can be formed with the above first semiconductor layer **131**, second semiconductor layer **132**, and third semiconductor layer **133**. Further, the third semiconductor layer **133**, which is a semiconductor layer having i-type conductivity that is obtained by a mixture of the semiconductor layer having n-type conductivity and the semiconductor layer having p-type conductivity, contributes to photoelectric conversion as a light-absorbing layer.

[0047] A low-resistance metal such as silver, aluminum, or copper can be used for the second electrode **120** and can be formed by a sputtering method, a vacuum evaporation method, or the like. Alternatively, the second electrode **120** may be formed using a conductive resin such as a silver paste or a copper paste by a screen printing method. As described above, the second electrode **120** can also be formed using a light-transmitting conductive film.

[0048] Note that the semiconductor layer having p-type conductivity that serves as a window layer may have a two-layer structure as illustrated in FIG. 4. The photoelectric conversion device illustrated in FIG. 4 includes, over a light-transmitting substrate **200**, a first electrode **210**, a first semiconductor layer **231**, a second semiconductor layer **232**, a third semiconductor layer **233**, a fourth semiconductor layer **234**, and a second electrode **220**.

[0049] For the substrate **200**, the first electrode **210**, the first semiconductor layer **231**, and the second electrode **220**, the same materials as the substrate **100**, the first electrode **110**, the first semiconductor layer **131**, and the second electrode **120** described in the structures of FIGS. 1A and 1B can be used, respectively.

[0050] Further, the third semiconductor layer **233** can be formed using the same material as the second semiconductor layer **132** described in the structures of FIGS. 1A and 1B, and the fourth semiconductor layer **234** can be formed using the same material as the third semiconductor layer **133** described therein.

[0051] The second semiconductor layer **232** includes an organic compound which exhibits p-type semiconductor characteristics, and any of the above materials which are given as examples of the organic semiconductor material having p-type conductivity can be used.

[0052] In such a manner, a process for forming a two-layer semiconductor layer having p-type conductivity that serves as a window layer can reduce the probability that a pinhole might be caused and a defect such as a short circuit between

upper and lower electrodes. Note that the structure of the photoelectric conversion device of FIG. 4 can also be combined with the structure of the photoelectric conversion device of FIG. 1B and/or the structure of the photoelectric conversion device of FIG. 2.

[0053] With the above structure, a photoelectric conversion device in which the amount of light loss caused by light absorption in a window layer is small and a short circuit between upper and lower electrodes is unlikely to occur can be provided.

[0054] This embodiment can be freely combined with any of the other embodiments.

Embodiment 2

[0055] In this embodiment, the light-transmitting semiconductor layer described in Embodiment 1 will be described.

[0056] For the light-transmitting semiconductor layer (first semiconductor layer **131**) in any of the photoelectric conversion devices described in Embodiment 1, a composite material of a transition metal oxide and an organic compound can be used. Note that in this specification, the word "composite" means not only a state in which two materials are simply mixed but also a state in which a plurality of materials is mixed and charges are transferred between the materials.

[0057] As the transition metal oxide, a transition metal oxide having an electron-accepting property can be used. Among transition metal oxides, an oxide of a metal belonging to any of Groups 4 to 8 of the periodic table, whose band gap is greater than or equal to 2 eV, preferably greater than or equal to 3 eV, is used.

[0058] For example, as the transition metal oxide, a vanadium oxide, a niobium oxide, a tantalum oxide, a chromium oxide, a molybdenum oxide, a tungsten oxide, a manganese oxide, a rhenium oxide, or a titanium oxide which has high electron-accepting property can be used. Among these, a molybdenum oxide is particularly preferable because of its stability in the air, low hygroscopic property, and easiness to be treated.

[0059] It is preferable to use, for the organic compound, a material whose band gap (a difference between the highest occupied molecular orbital (HOMO level) and the lowest unoccupied molecular orbital level (LUMO level)) is greater than or equal to 2 eV, preferably greater than or equal to 3 eV.

[0060] The organic compound preferably has a high hole-transport property. Specifically, a substance having a hole mobility higher than or equal to 10^{-6} cm²/Vs is preferably used. Note that other than the above substance, any substance that has a property of transporting more holes than electrons may be used.

[0061] For example, as the organic compound, any of a variety of compounds such as an aromatic amine compound, a carbazole derivative, an aromatic hydrocarbon, a high molecular compound (e.g., an oligomer, a dendrimer, or a polymer), and a heterocyclic compound having a dibenzofuran skeleton or a dibenzothiophene skeleton can be used.

[0062] With the use of the inorganic compound and organic compound described above, a composite material having a high light-transmitting property can be formed.

[0063] In a composite material of the above-described transition metal oxide and the above-described organic compound, electrons in the highest occupied molecular orbital level (HOMO level) of the organic compound are transferred to the conduction band of the transition metal oxide, whereby interaction between the transition metal oxide and the organic

compound occurs. Due to this interaction, the composite material including the transition metal oxide and the organic compound has high carrier concentration and has p-type semiconductor characteristics.

[0064] The organic compounds which can be used for the composite material will be specifically enumerated below.

[0065] As the aromatic amine compounds that can be used for the composite material, the following can be given as examples: 4,4'-bis[N-(1-naphthyl)-N-phenylamino]biphenyl (abbreviation: NPB); N,N'-bis(3-methylphenyl)-N,N'-diphenyl-[1,1'-biphenyl]-4,4'-diamine (abbreviation: TPD); 4,4',4''-tris(N,N-diphenylamino)triphenylamine (abbreviation: TDATA); 4,4',4''-tris[N-(3-methylphenyl)-N-phenylamino]triphenylamine (abbreviation: MTDATA); and N,N'-bis(spiro-9,9'-bifluoren-2-yl)-N,N'-diphenylbenzidine (abbreviation: BSPB). In addition, the following can be given: N,N'-bis(4-methylphenyl)-N,N'-diphenyl-p-phenylenediamine (abbreviation: DTDPPA); 4,4'-bis[N-(4-diphenylaminophenyl)-N-phenylamino]biphenyl (abbreviation: DPAB); N,N'-bis{4-[bis(3-methylphenyl)amino]phenyl}-N,N'-diphenyl-(1,1'-biphenyl)-4,4'-diamine (abbreviation: DNTPD); 1,3,5-tris[N-(4-diphenylaminophenyl)-N-phenylamino]benzene (abbreviation: DPA3B); 4-phenyl-4'-(9-phenylfluoren-9-yl)triphenylamine (abbreviation: BPAFLP); 4,4'-bis[N-(9,9-dimethylfluoren-2-yl)-N-phenylamino]biphenyl (abbreviation: DFLDPBi); and 4,4'-bis[N-(spiro-9,9'-bifluoren-2-yl)-N-phenylamino]biphenyl (abbreviation: BSPB).

[0066] As carbazole derivatives which can be used for the composite material, the following can be given as specific examples: 3-[N-(9-phenylcarbazol-3-yl)-N-phenylamino]-9-phenylcarbazole (abbreviation: PCzPCA1); 3,6-bis[N-(9-phenylcarbazol-3-yl)-N-phenylamino]-9-phenylcarbazole (abbreviation: PCzPCA2); and 3-[N-(1-naphthyl)-N-(9-phenylcarbazol-3-yl)amino]-9-phenylcarbazole (abbreviation: PCzPCN1).

[0067] Moreover, as another carbazole derivative which can be used for the composite material, 4,4'-di(N-carbazolyl)biphenyl (abbreviation: CBP), 1,3,5-tris[4-(N-carbazolyl)phenyl]benzene (abbreviation: TCPB), 9-[4-(N-carbazolyl)phenyl]-10-phenylanthracene (abbreviation: CzPA), 1,4-bis[4-(N-carbazolyl)phenyl]-2,3,5,6-tetraphenylbenzene, or the like can be used.

[0068] As aromatic hydrocarbon that can be used for the composite material, the following can be given as examples: 2-tert-butyl-9,10-di(2-naphthyl)anthracene (abbreviation: t-BuDNA); 2-tert-butyl-9,10-di(1-naphthyl)anthracene; 9,10-bis(3,5-diphenylphenyl)anthracene (abbreviation: DPPA); 2-tert-butyl-9,10-bis(4-phenylphenyl)anthracene (abbreviation: t-BuDBA); 9,10-di(2-naphthyl)anthracene (abbreviation: DNA); 9,10-diphenylanthracene (abbreviation: DPAnth); 2-tert-butylanthracene (abbreviation: t-BuAnth); 9,10-bis(4-methyl-1-naphthyl)anthracene (abbreviation: DMNA); 9,10-bis[2-(1-naphthyl)phenyl]-2-tert-butylanthracene; 9,10-bis[2-(1-naphthyl)phenyl]anthracene; 2,3,6,7-tetramethyl-9,10-di(1-naphthyl)anthracene; 2,3,6,7-tetramethyl-9,10-di(2-naphthyl)anthracene; 9,9'-bianthryl; 10,10'-diphenyl-9,9'-bianthryl; 10,10'-bis(2-phenylphenyl)-9,9'-bianthryl; 10,10'-bis[(2,3,4,5,6-pentaphenyl)phenyl]-9,9'-bianthryl; anthracene; tetracene; rubrene; perylene; and 2,5,8,11-tetra(tert-butyl)perylenene. Besides those, pentacene, coronene, or the like can also be used. The aromatic hydrocarbon which has a hole mobility higher than or equal to 1×10^{-6} cm²/Vs and which has 14 to 42 carbon atoms is particularly preferable.

[0069] The aromatic hydrocarbon which can be used for the composite material may have a vinyl skeleton. As the aromatic hydrocarbon having a vinyl group, the following are given as examples: 4,4'-bis(2,2-diphenylvinyl)biphenyl (abbreviation: DPVBi) and 9,10-bis[4-(2,2-diphenylvinyl)phenyl]anthracene (abbreviation: DPVPA).

[0070] The organic compound used for the composite material may be a heterocyclic compound having a dibenzofuran skeleton or a dibenzothiophene skeleton.

[0071] The organic compound that can be used for the composite material may be a high molecular compound, and the following can be given as examples: poly(N-vinylcarbazole) (abbreviation: PVK); poly(4-vinyltriphenylamine) (abbreviation: PVTPA); poly[N-(4-{N'-[4-(4-diphenylamino)phenyl]phenyl-N'-phenylamino}phenyl)methacrylamide] (abbreviation: PTPDMA); and poly[N,N'-bis(4-butylphenyl)-N,N'-bis(phenyl)benzidine] (abbreviation: Poly-TPD).

[0072] A variety of methods can be used for forming the light-transmitting semiconductor layer, whether the method is a dry process or a wet process. As a dry method, a codeposition method, by which a plurality of evaporation materials is vaporized from a plurality of evaporation sources to perform deposition, is given as an example. As a wet method, a composition having a composite material is adjusted by a sol-gel method or the like, and deposition can be performed using an ink-jet method or a spin-coating method.

[0073] When the above-described light-transmitting semiconductor layer is used for a window layer of a photoelectric conversion device, the light loss caused by light absorption in the window layer is reduced, and the electric characteristics of the photoelectric conversion device can be improved. The window layer can be formed thick because of a high light-transmitting property and low resistance, which enables a photoelectric conversion device in which a short circuit between upper and lower electrodes is unlikely to occur.

[0074] This embodiment can be freely combined with any of the other embodiments.

[0075] This application is based on Japanese Patent Application serial No. 2011-195372 filed with the Japan Patent Office on Sep. 7, 2011, the entire contents of which are hereby incorporated by reference.

What is claimed is:

1. A photoelectric conversion device comprising:

- a substrate;
 - a first electrode over the substrate;
 - a light-transmitting semiconductor layer over the first electrode;
 - a first semiconductor layer over the light-transmitting semiconductor layer;
 - a second semiconductor layer over the first semiconductor layer; and
 - a second electrode over the second semiconductor layer,
- wherein the light-transmitting semiconductor layer includes an organic compound and an inorganic compound.

2. The photoelectric conversion device according to claim 1, wherein the light-transmitting semiconductor layer has p-type conductivity, the first semiconductor layer has i-type conductivity, and the second semiconductor layer has n-type conductivity.

3. The photoelectric conversion device according to claim 1, wherein the inorganic compound is selected from a transition metal oxide.

4. The photoelectric conversion device according to claim 1, wherein the inorganic compound is an oxide of a metal belonging to any of Group 4 to Group 8 in the periodic table.

5. The photoelectric conversion device according to claim 1, wherein the inorganic compound is selected from a vanadium oxide, a niobium oxide, a tantalum oxide, a chromium oxide, a molybdenum oxide, a tungsten oxide, a manganese oxide, a rhenium oxide, and a titanium oxide.

6. The photoelectric conversion device according to claim 1, wherein the organic compound is selected from an aromatic amine compound, a carbazole derivative, an aromatic hydrocarbon, a high molecular compound, and a heterocyclic compound having a dibenzofuran skeleton or a dibenzothiophene skeleton.

7. A photoelectric conversion device comprising:

a substrate;

a first electrode over the substrate;

a first light-transmitting semiconductor layer over the first electrode;

a second light-transmitting semiconductor layer over the first light-transmitting semiconductor layer;

a first semiconductor layer over the second light-transmitting semiconductor layer;

a second semiconductor layer over the first semiconductor layer; and

a second electrode over the second semiconductor layer, wherein the first light-transmitting semiconductor layer includes an organic compound and an inorganic compound, and

wherein the second light-transmitting semiconductor layer includes an organic compound.

8. The photoelectric conversion device according to claim 7, wherein the first light-transmitting semiconductor layer and the second light-transmitting semiconductor layer have p-type conductivity, the first semiconductor layer has i-type conductivity, and the second semiconductor layer has n-type conductivity.

9. The photoelectric conversion device according to claim 7, wherein the inorganic compound is selected from a transition metal oxide.

10. The photoelectric conversion device according to claim 7, wherein the inorganic compound is an oxide of a metal belonging to any of Group 4 to Group 8 in the periodic table.

11. The photoelectric conversion device according to claim 7, wherein the inorganic compound is selected from a vanadium oxide, a niobium oxide, a tantalum oxide, a chromium oxide, a molybdenum oxide, a tungsten oxide, a manganese oxide, a rhenium oxide, and a titanium oxide.

oxide, a niobium oxide, a tantalum oxide, a chromium oxide, a molybdenum oxide, a tungsten oxide, a manganese oxide, a rhenium oxide, and a titanium oxide.

12. The photoelectric conversion device according to claim 7, wherein the organic compound is selected from an aromatic amine compound, a carbazole derivative, an aromatic hydrocarbon, a high molecular compound, and a heterocyclic compound having a dibenzofuran skeleton or a dibenzothiophene skeleton.

13. A photoelectric conversion device comprising:

a substrate;

a first electrode over the substrate;

a first semiconductor layer over the first electrode;

a second semiconductor layer over the first semiconductor layer;

a light-transmitting semiconductor layer over the second semiconductor layer; and

a second electrode over the light-transmitting semiconductor layer,

wherein the light-transmitting semiconductor layer includes an organic compound and an inorganic compound.

14. The photoelectric conversion device according to claim 13, wherein the light-transmitting semiconductor layer has p-type conductivity, the first semiconductor layer has i-type conductivity, and the second semiconductor layer has n-type conductivity.

15. The photoelectric conversion device according to claim 13, wherein the inorganic compound is selected from a transition metal oxide.

16. The photoelectric conversion device according to claim 13, wherein the inorganic compound is an oxide of a metal belonging to any of Group 4 to Group 8 in the periodic table.

17. The photoelectric conversion device according to claim 13, wherein the inorganic compound is selected from a vanadium oxide, a niobium oxide, a tantalum oxide, a chromium oxide, a molybdenum oxide, a tungsten oxide, a manganese oxide, a rhenium oxide, and a titanium oxide.

18. The photoelectric conversion device according to claim 13, wherein the organic compound is selected from an aromatic amine compound, a carbazole derivative, an aromatic hydrocarbon, a high molecular compound, and a heterocyclic compound having a dibenzofuran skeleton or a dibenzothiophene skeleton.

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